

## Oxidation of Alcohols with Sodium Periodate Catalyzed by Supported Mn(III) Porphyrins

M. Moghadam<sup>a,\*</sup>, S. Tangestaninejad<sup>b</sup>, V. Mirkhani<sup>b</sup>, B. Karami<sup>a</sup>, N. Rashidi<sup>a</sup> and H. Ahmadi<sup>a</sup>

<sup>a</sup>Department of Chemistry, Yasouj University, Yasouj 75914-353, Iran

<sup>b</sup>Department of Chemistry, Isfahan University, Isfahan 81746-73441, Iran

(Received 11 September 2005, Accepted 28 December 2005)

The mild and efficient oxidation of alcohols with sodium periodate catalyzed by manganese(III) tetrakis(*p*-sulfonato-phenylporphyrinato) acetate, [Mn(TPPS)], supported on polyvinylpyridine, [Mn(TPPS)-PVP], and Amberlite IRA-400, [Mn(TPPS)-Ad IRA-400], at room temperature is reported. The catalysts used in this study showed high activity not only in the oxidation of benzylic and linear alcohols but also in the oxidation of secondary alcohols at room temperature. These catalysts can be reused several times without significant loss of their activity.

**Keywords:** Biomimetic, Alcohols, Supported metalloporphyrins, Periodate

---

### INTRODUCTION

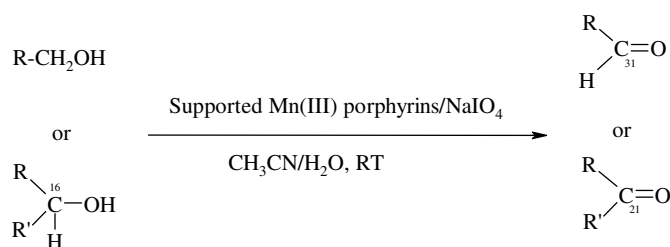
Metalloporphyrins have been successfully used as models for the cytochrome P-450 enzyme with respect to the oxidation of organic compounds such as hydrocarbons [1-3]. Development in this area is based on different strategies with the aim of designing selective and stable catalytic systems with high turnover [4]. It was found that when metalloporphyrins were used as catalysts, organic compounds could be oxidized by oxygen donors such as PhIO, ClO<sup>-</sup>, H<sub>2</sub>O<sub>2</sub>, ROOH or IO<sub>4</sub><sup>-</sup> [5-11]. However, these expensive catalysts were difficult to recover and unstable, which limited their application in synthetic chemistry. Heterogenization of these homogeneous catalysts stabilizes the metalloporphyrin or enhances the catalytic performance by preventing the formation of inactive dimers. On the other hand, such immobilization can influence the chemoselectivity, regioselectivity and stereoselectivity of the catalyzed reaction [12-16].

Moreover, the heterogenized metalloporphyrins have several practical advantages over homogeneous catalysts such as the facilitation of catalyst separation from the reaction mixture, simplification of the procedures for recycling the catalyst and the possibility of adaptation of the immobilized catalyst for a continuous flow process. The main approaches for attachment of metalloporphyrins onto solid supports are: (i) binding through electrostatic interaction, (ii) covalently bonding to substituents on the support in *meso*aryl positions, (iii) intercalation or entrapment of the porphyrin between the layers of clay or within the pores or matrices of solids, and (iv) coordinative binding between the supports and the porphyrin metal center.

Immobilized oxidation catalysts have been developed that are supported on organic and inorganic polymers, silica gel and metal oxides. These heterogeneous catalysts can be recovered from the reaction media by simple filtration and reused. They also increase the selectivity without contaminating the product solution. As the transition metal complexes are expensive or difficult to purchase,

---

\*Corresponding author. E-mail: moghadamm@mail.yu.ac.ir



Scheme 1

immobilizing them on a support allows them to be simply extracted and recycled, which makes for commercial advantage as well as ease of manipulation.

The successful application of these supported manganese(III) porphyrin/periodate systems in the epoxidation of alkenes and hydroxylation of alkanes [17,18], and our interest in supported metalloporphyrins in catalysis [19-25], prompted us to investigate the use of these supported catalysts in the oxidation of alcohols with sodium periodate at room temperature in a 1:1 CH<sub>3</sub>CN:H<sub>2</sub>O mixture (Scheme 1).

## EXPERIMENTAL

All materials were of commercial reagent grade. Alcohols were obtained from Merck or Fluka. Mn(TPPS) was prepared, metalated, and supported as previously published [26-29]. FT-IR spectra were obtained using potassium bromide pellets in the range of 400-4000 cm<sup>-1</sup> with a Nicolet Impact 400D spectrometer. Gas chromatography (GC) experiments were performed with a Shimadzu GC-16A gas chromatograph using a 2 m column packed with silicon DC-200 or Carbowax 20 M. <sup>1</sup>H NMR spectra were recorded on a 300 MHz Bruker-Avance AQS spectrometer.

### Typical Procedure for Oxidation of Alcohols with NaIO<sub>4</sub> Catalyzed by Supported Mn(III) Porphyrins

All of the reactions were carried out at room temperature in a 25 ml flask equipped with a magnetic stirrer bar. A solution of NaIO<sub>4</sub> (2 mmol) in H<sub>2</sub>O (10 ml) was added to a mixture of alcohol (1 mmol), supported Mn(III) porphyrins (20 μmol) and imidazole (0.2 mmol) in CH<sub>3</sub>CN (10 ml). The progress of the reaction was monitored by GLC. The reaction mixture was filtered and diluted with water (20 ml). The

products were extracted with CH<sub>2</sub>Cl<sub>2</sub> (2 × 10 ml) and were purified on silica-gel plates or a silica-gel column (CCl<sub>4</sub>-Et<sub>2</sub>O, 4:1). IR and <sup>1</sup>H NMR spectral data was used to confirm the identities of the products.

### Catalyst Reuse and Stability

The stability of supported Mn(III) porphyrins were studied in four consecutively repeated oxidation reactions. The oxidation of benzyl alcohol was chosen as a model substrate for studying the reuse and stability of catalysts. The reactions were carried out as described above. When each of the repeated reactions was completed, the catalysts were recovered by filtration, washed exhaustively with water, methanol, acetonitrile and diethyl ether, successively, and dried before being reused with fresh benzyl alcohol and sodium periodate. The amount of manganese that leached into the filtrates was determined by atomic absorption spectrometry.

## RESULTS AND DISCUSSION

### Oxidation of Alcohols with Sodium Periodate Catalyzed by Supported Mn (TPPS)

We first investigated the ability of these supported manganese(III) porphyrins as catalysts in the oxidation of benzyl alcohol in the presence of sodium periodate. Of the four solvents tested, including 1:1 mixtures of methanol, ethanol, acetone, and acetonitrile with water, the 1:1 acetonitrile/water mixture was chosen as the solvent because it gave a higher carbonyl yield.

An investigation of the effect of different axial ligands on the oxidation rate of benzyl alcohol revealed that imidazole was the most efficient. The optimum proportions used for the oxidation of benzyl alcohol with these heterogenized systems was a catalyst:oxidant:imidazole:substrate molar ratio of 1:100:10:50. After using the catalysts two times, the reaction solutions remained colorless and there was no evidence of leaching of the catalyst from supports into solution. This was confirmed by examining the UV-Vis spectra of the filtered reaction mixtures (Table 1).

This heterogeneous catalyst can be applied to reactions using a wide variety of primary and secondary alcohols. As shown in Table 2, benzyl alcohol and substituted benzyl

## Oxidation of Alcohols with Sodium Periodate

**Table 1.** Catalyst Reuse and Stability after Consecutive Runs of Oxidation of Benzyl Alcohol

Run	Mn(TPPS)-Ad IRA-400		Mn(TPPS)-PVP	
	Yield (%) <sup>a</sup>	Mn leached (%) <sup>b</sup>	Yield (%) <sup>a</sup>	Mn leached (%) <sup>b</sup>
1	95	2.2	95	1.8
2	92	1.5	93	1.2
3	90	0	91	0
4	90	0	90	0

<sup>a</sup>GLC yield based on starting alcohol. <sup>b</sup>Determined by atomic absorption spectroscopy.

**Table 2.** Performance of Catalysts in the Oxidation of Alcohols with NaIO<sub>4</sub>

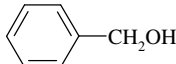
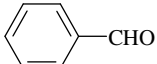
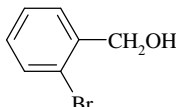
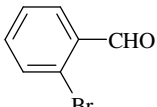
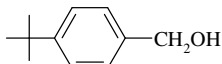
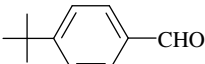
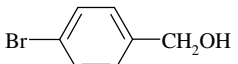
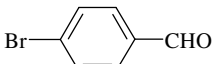
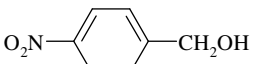
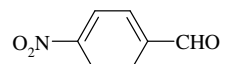
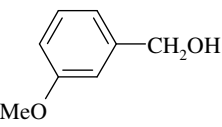
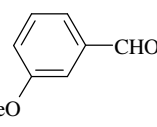
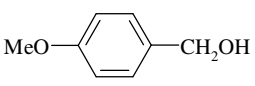
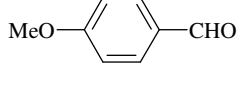
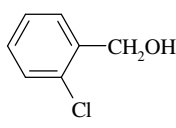
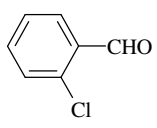
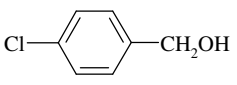
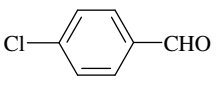
Entry	Alcohol	Product	Mn(TPPS)-Ad-IRA 400		Mn(TPPS)-PVP	
			Time (h)	Yield (%) <sup>a</sup>	Time (h)	Yield (%) <sup>a</sup>
1			5	95	5	95
2			4.5	85	4	83
3			4.5	81	4	80
4			3.5	90	3.5	90
5			7.5	85	7	85
6			5.5	91	5	90
7			5.5	90	5	90
8			4	90	4.5	92
9			4.5	98	4.5	99

Table 2. Continued

10			8	95	7.5	95
11			5	80	4.8	82
12			5.6	90	6	92
13			7	95	6.5	95
14			6	80	6.5	80
15			8	75	7.5	77
16			8	78	7.5	78
17			5.5	80	6	82
18			5	83	5	84
19			8	69	7.5	70
20			7	90	6.5	91
21			7	85	7	88

<sup>a</sup>GLC yield based on starting alcohol.

alcohols are converted to their corresponding aldehydes efficiently. The results show that the substituents have no significant effect on the oxidation of benzylic alcohols. Linear

alcohols were oxidized efficiently with  $\text{NaIO}_4$  by these supported catalysts. These heterogenized catalysts were also used for the oxidation of secondary alcohols; their

corresponding ketones were obtained in good yields.

### Catalyst Reuse and Stability

The stability of the supported catalysts was monitored using multiple sequential oxidations of benzyl alcohol with sodium periodate. After the catalysts were reused four consecutive times, the benzaldehyde yield was still 90% (Table 1).

These supported manganese porphyrins can be used as robust, reusable and active heterogeneous catalysts in the oxidation of primary and secondary alcohols with sodium periodate.

### ACKNOWLEDGMENT

The financial support of this work by Yasouj University Research Council is acknowledged.

### REFERENCES

- [1] B. Meunier, *Chem. Rev.* 92 (1992) 1411.
- [2] R.A. Sheldon (Ed.), *In Metalloporphyrins in Catalytic Oxidations*, Marcel Dekker, New York, 1994.
- [3] B. Meunier, A. Robert, G. Pratviel, J. Bernadou, in: K. Kadish, K.M. Smith, R. Guilard (Eds.), *The Porphyrins Handbook*, Vol. 4, Academic Press, New York, London, 2000.
- [4] R.A. Sheldon, in: B. Meunier (Ed.), *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*, Imperial College Press, London, 2000.
- [5] M.J. Coon, R.E. White, in: T.G. Spiro (Ed.), *Dioxygen Binding and Activation by Metal Centers*, Wiley, New York, 1980, Chapter 2.
- [6] R.E. White, M. Coon, *J. Annu. Rev. Biochem.* 49 (1980) 315.
- [7] J.T. Groves, T.E. Nemo, *J. Am. Chem. Soc.* 105 (1983) 5786.
- [8] O. Bortolini, B. Meunier, *J. Chem. Soc. Perkin Trans. 2* (1984) 1967.
- [9] B. Meunier, E. Guilmet, M.E. De Carvalho, R. Poilblanc, *J. Am. Chem. Soc.* 106 (1984) 6668.
- [10] D. Mohajer, S. Tangestaninejad, *J. Chem. Soc. Chem. Commun.* (1993) 240.
- [11] D. Mohajer, S. Tangestaninejad, *Tetrahedron Lett.* 35 (1994) 945.
- [12] H. Turk, W.T. Ford, *J. Org. Chem.* 56 (1990) 1253.
- [13] L. Barloy, P. Battioni, D. Mansuy, *J. Chem. Soc. Chem. Commun.* (1990) 1365.
- [14] F. Pautet, M. Daudon, *Tetrahedron Lett.* 32 (1991) 1457.
- [15] D.R. Leonard, J.R. Lindsay Smith, *J. Chem. Soc. Perkin Trans. 2* (1990) 1917
- [16] D.R. Leonard, J.R. Lindsay Smith, *J. Chem. Soc. Perkin Trans. 2* (1991) 25.
- [17] S. Tangestaninejad, V.J. Mirkhani, *Chem. Res. (S)* (1998) 788.
- [18] S. Tangestaninejad, M.H. Habibi, V. Mirkhani, M. Moghadam, *Molecules* 7 (2002) 264.
- [19] S. Tangestaninejad, M. Moghadam, *J. Chem. Res. (S)* (1998) 242.
- [20] S. Tangestaninejad, M. Moghadam, *Synth. Commun.* 28 (1998) 427.
- [21] V. Mirkhani, S. Tangestaninejad, M. Moghadam, *J. Chem. Res. (S)* (1999) 722.
- [22] S. Tangestaninejad, M.H. Habibi, V. Mirkhani, M. Moghadam, *J. Chem. Res. (S)* (2001) 444.
- [23] V. Mirkhani, S. Tangestaninejad, M. Moghadam, Z. Karimian, *Bioorg. Med. Chem. Lett.* 13 (2003) 3433.
- [24] V. Mirkhani, S. Tangestaninejad, M. Moghadam, Z. Karimian, *J. Chem. Res. (S)* (2003) 792.
- [25] M. Moghadam, S. Tangestaninejad, M.H. Habibi, V. Mirkhani, *J. Mol. Catal. A: Chemical* 217 (2004) 9.
- [26] M. Moghadam, S. Tangestaninejad, V. Mirkhani, I. Mohammadpoor-Baltork, H. Kargar, *Bioorg. Med. Chem.* 13 (2005) 2901.
- [27] A. Harriman, G. Porter, *J. Chem. Soc. Faraday Trans. II* 75 (1979) 1532.
- [28] E.B. Fleischer, J.M. Palmer, T.S. Srinivastava, A. Chatterjee, *J. Am. Chem. Soc.* 93 (1971) 3162.
- [29] Y. Saito, M. Mifume, S. Nakashima, H. Nakayama, J. Odo, Y. Tanaka, M. Chikuma, H. Tanaka, *Chem. Pharm. Bull.* 34 (1987) 2885.